843. *The Reactions of Hydroxyl Radicals with Hydrocarbons in Aqueous Solution.*

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The relative reactivities of methane, ethane, propane, n-butane, isobutane, and cyclopropane with hydroxyl radicals produced by the photolysis of hydrogen peroxide and nitric acid have been determined by a method which depends on the study of the rate of consumption of two hydrocarbons. Incidentally the solubilities of the hydrocarbons in aqueous media have also been determined. Hydroxyl radicals in solution at 17·5° react in the same way as chlorine atoms in the gas phase at 25°.

TRANSFER reactions of hydroxyl radicals with most hydrocarbons, $\cdot OH + RH = H_2O + R\cdot$, are exothermic to the extent of 20 kcal. mole^{-1} or more. They might therefore be expected to have low activation energies, probably similar to those of reactions of chlorine or even fluorine atoms. The only studies of these reactions that have been reported are considered to be of doubtful reliability.[1] They indicate [2] that the activation energies are as high as 7—10 kcal. mole^{-1}. These high values are supported by the more reliable work on the reaction with hydrogen which has been studied directly and as a step in the hydrogen–oxygen reaction.[3,4]

The reactions have here been studied for the liquid phase because it was simpler to generate hydroxyl radicals in that medium than in the gas phase, although in all other ways this procedure introduced complications. Hydroxyl radicals were produced by the photolysis of both hydrogen peroxide and nitric acid: they then reacted with the mixture of dissolved hydrocarbons:

$$\cdot OH + R^1H = H_2O + R^1\cdot \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$\cdot OH + R^2H = H_2O + R^2\cdot \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

The alkyl radicals were removed to a small extent by combination and by reaction with dissolved oxygen. k_1/k_2 can be found from measurements of the relative rates of consumption of the hydrocarbons.

Let v_{t1} be the total volume of hydrocarbon 1 in the reaction system measured in c.c. at N.T.P., v_{g1} be the volume in the gas phase, and v_{l1} be the volume in solution. Then, if V_g is the volume of the gas phase, V_l the volume of the liquid phase, T the temperature, and α_1 is Bunsen's absorption coefficient, we have

$$v_{l1} = \alpha_1 V_l (v_{g1}/V_g)(T/273).$$

Therefore,
$$v_{t1} = v_{g1}[1 + \alpha_1 (V_l/V_g)(T/273)].$$

Hence
$$v_{l1} = v_{t1}\{1 - 1/[1 + \alpha_1 (V_l/V_g)(T/273)]\}$$
$$\equiv K_1 v_{t1}.$$

Now, provided that equilibrium between the liquid and the gas phase is maintained during the reaction, we have

$$-d(v_{t1})/dt = k_1'[OH]v_{l1} = k_1'K_1[OH]v_{t1},$$
$$-d(v_{t2})/dt = k_2'[OH]v_{l2} = k_2'K_2[OH]v_{t2},$$

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[1] Steacie, "Atomic and Free Radical Reactions," 2nd edn., Rheinhold Publ. Corp., New York, 1954, p. 606.

[2] Avramenko and Lorentzo, *Doklady Akad. Nauk S.S.S.R.*, 1949, **67**, 867.

[3] Avramenko and Lorentzo, *Zhur. fiz. Khim.*, 1950, **24**, 207; see also Trotman-Dickenson, *Chem. and Ind.*, 1959, 1159.

[4] Dainton and Hardwick, *Trans. Faraday Soc.*, 1957, **53**, 333.

Where the primes indicate that the units of the rate constants are a function of the dimensions of the system. From these equations we derive

$$\frac{k_1K_1}{k_2K_2} = \frac{\log\,(v_{t1})_{\mathrm{i}} - \log\,(v_{t1})_{\mathrm{f}}}{\log\,(v_{t2})_{\mathrm{i}} - \log\,(v_{t2})_{\mathrm{f}}}$$

Where the subscripts i and f indicate the initial and the final amounts of the reactants. It may be noted that because the absorption coefficients of hydrocarbons in aqueous solutions are very low, K_1/K_2 is nearly equal to α_1/α_2. Surprisingly, the solubilities of very few gaseous hydrocarbons in water have been reported; these had therefore to be determined.

EXPERIMENTAL

Materials.—The hydrocarbons were obtained from cylinders and degassed. The iodine, hydrogen peroxide, and perchloric and nitric acid were of " AnalaR " grade. Ordinary distilled water was used.

Determination of Rate Constants.—A quartz cylindrical reaction vessel (7 c.c.; 6 cm. long) was filled with a solution of hydrogen peroxide or nitric acid until an air-space of about 2 c.c. remained. This vessel terminated in a length of narrow quartz tubing and a ground joint. The vessel was attached to the vacuum system, then cooled in liquid nitrogen, and evacuated. After measured quantities of two hydrocarbons from a gas burette had been condensed on top of the solution the vessel was sealed and allowed to warm. The dead space was small, so that when methane was used the amount in the vessel could be accurately estimated.

The vessel was then attached to a Vibro shaker so that it was shaken horizontally, breaking the surface of a water bath through which tap water flowed. It was irradiated by the full light from a medium-pressure mercury arc for 1—2 hr. At the end of the run the vessel was marked with a file and placed in a rubber-and-glass tube. The tube was evacuated and the neck of the vessel broken. Several trials were required before a suitable device for opening the quartz vessel was found. In the early designs the containing tube was frequently broken by the vessel which was propelled by the stream of high-pressure gas surging out of it. All the liquid was distilled out of the vessel into two traps cooled in alcohol–solid carbon dioxide. The gases were collected in a trap (attached to the chromatography apparatus) which was cooled in liquid nitrogen. Several distillations of the aqueous mixture were needed to ensure that all the hydrocarbons were liberated. Control runs showed that the procedure was satisfactory. A special Toepler pump and a pump-down trap were used in handling methane.

The gases were analysed on a gas–solid chromatographic apparatus with a Janak nitrometer detector. The columns were of alumina (40—60 mesh), poisoned with 1·5% of squalane, except for the separation of methane which required an activated charcoal column.

Determination of Solubilities.—A suitable volume of a hydrocarbon, measured on a gas burette, was introduced into a vessel of known volume, placed in a thermostat bath and containing a known volume of liquid which was stirred. The pressure in the system was measured after sufficient time (1—2 hr.) for establishment of equilibrium. As the pressure was read before and after the introduction of the gas there was no need completely to degass the liquid. This simple procedure with a vessel of 784 c.c. filled with 684 c.c. of liquid yielded results that were reproducible to ±1%. The values found for Bunsen's absorption coefficient at 17·5° are:

	$10^4\alpha$			$10^4\alpha$	
Hydrocarbon	Water	0·5N-HNO_3	Hydrocarbon	Water	0·5N-HNO_3
Methane	416 ± 15	—	Cyclopropane	—	379 ± 1
Ethane	679 ± 5	648 ± 2	*n*-Butane	471 ± 5	—
Propane	543	534	Isobutane	355 ± 4	—

RESULTS AND DISCUSSION

Table 1 lists results obtained with n-butane–propane mixtures when iodine and large quantities of oxygen were added to the system to remove alkyl radicals as they were formed. The additives do not alter the results. The results obtained for isobutane–propane (Table 2) with hydrogen peroxide [*k*(isobutane)/*k*(propane) = 1·02] and with nitric acid (*k* ratio = 1·12) differ by little more than the experimental errors. A medium effect probably slightly alters the relative rates of identical reactions. Since no detailed studies of the photolysis of nitric acid have been reported, the similarity of the results with the peroxide and the acid are relied on as evidence that the acid splits into hydroxyl and nitrogen dioxide (which seems the most likely primary act). Hydroxyl radicals are known to be formed by photolysis of the peroxide [4] and are the only radicals that could also be formed from the acid. Some HO_2· must be formed by the reaction of hydroxyl with the peroxide,[4] but as its reactivity is thought to be considerably lower than that of hydroxyl it should not affect the consumption of hydrocarbon.

TABLE 1.

Reaction of hydroxyl radicals with n-butane–propane mixtures at 17·5°.

n-Butane (c.c. at N.T.P.)		Propane (c.c. at N.T.P.)		Medium		$\frac{k(\text{n-butane})}{k(\text{propane})}$
				H_2O_2	$HClO_4$	
Initial	Final	Initial	Final	(M)	(M)	
4·03	1·82	6·54	3·32	0·9	0·02 [a]	1·35
4·18	2·73	6·60	4·59	0·1	0·10 [a]	1·35
4·20	3·02	5·42	4·08	0·3	0·03 [a]	1·33
4·20	2·22	4·33	2·47	0·9	0·02 [b]	1·31
4·67	2·56	4·60	2·72	0·9	0·02	1·32
5·91	4·70	4·86	4·05	0·08	0·08 [a,b]	1·41
5·62	1·99	3·27	1·29	0·9	0·02 [a]	1·29
6·47	2·48	2·88	1·19	0·9	0·02 [a]	1·25

[a] In presence of 1 atm. of oxygen. In presence of iodine.

TABLE 2.

Reaction of hydroxyl radicals with isobutane–propane mixtures at 17·5°.

Isobutane (c.c. at N.T.P.)		Propane (c.c. at N.T.P.)		Medium			$\frac{k(\text{isobutane})}{k(\text{propane})}$
				H_2O_2	HNO_3	$HClO_4$	
Initial	Final	Initial	Final	(M)	(M)	(M)	
2·85	2·02	6·47	3·86	0·6	—	0·07	1·03
6·13	5·58	6·20	5·36	0·2	—	0·02	1·00
6·56	4·84	6·56	4·06	0·6	—	0·07	1·00
5·93	4·30	5·92	3·57	0·6	—	0·07	0·98
6·64	5·89	3·01	2·51	0·2	—	0·02	1·06
6·29	4·27	2·84	1·59	0·6	—	0·07	1·03
						Mean =	1·02 ± 0·03
3·52	2·47	7·15	4·44	—	0·5	—	1·13
4·91	3·25	7·38	4·19	—	0·5	1	1·12
3·34	2·06	3·68	1·98	—	0·5	—	1·19
6·66	4·92	6·69	4·32	—	0·5	1	1·06
6·37	4·67	6·28	3·99	—	0·5	—	1·06
5·20	4·20	4·75	3·59	—	0·5	2	1·17
6·80	4·06	3·57	1·75	—	0·5	1	1·10
6·89	4·26	3·47	1·85	—	0·5	—	1·17
						Mean =	1·12 ± 0·06

TABLE 3.

Relative reactivities.

	Hydroxyl (17·5°, solution)	Chlorine atom (25°, gas)
Methane	0·42	0·0024
Ethane	1	1
Propane	2·78	2·71
Cyclopropane	0·18	0·0031
n-Butane	3·70	3·66
Isobutane	3·14	2·99

If this conclusion is accepted, then Table 3, which shows the relative reactivities of the hydrocarbons at 17·5°, shows our results with cyclopropane–methane–hydrogen peroxide, cyclopropane–propane–nitric acid, and propane–ethane–hydrogen peroxide.

The similarity of the relative reactivities of the alkanes, apart from methane, with the hydroxyl radicals and chlorine atoms is so marked that the absolute reactivities are probably also similar. This conclusion is supported by the general parallelism (Table 4) between high reactivity and low selectivity for small free radicals and by the way in which the present observations on hydroxyl fit the series.

The results indicate that the activation energies for the reactions of hydroxyl radicals with alkanes in aqueous solution are only 1—2 kcal. mole^{-1}. A hydroxyl radical is probably much more highly solvated than is the activated complex which it forms with an alkane. Therefore still greater reactivity would be expected in the gas phase. Russell[5] noted that solvated chlorine atoms were markedly more selective in their attack on hydrocarbons than were the atoms that reacted in the gas phase. More work will clearly be needed to resolve the disagreement between these results and those of Avramenko and his collaborators.

TABLE 4.

Relative reactivities of hydrogen atoms in various environments with various radicals, $X\cdot + RH \longrightarrow XH + R\cdot$.

Radical, X·	Methyl	Cyclopropyl	CH_3	CH_2	CH	*E*	Ref.
F (25°)	0·8	0·9	1	1·2	1·4	0·3	*a*
OH (17·5°)	0·6	0·18	1	4·7	9·8	—	*b*
Cl (25°)	0·004	0·003	1	4·6	8·9	1·0	*c*
CF_3 (182°)	0·08	—	1	6	36	7·5	*d*
MeO (230°)	—	0·35	1	8	27	7·1	*e*
Me (182°)	0·04	0·55	1	7	50	11	*f*
Br (98°)	0·002	—	1	250	6300	13·4	*g*

E is the activation energy for the attack of the radical on ethane, in kcal. mole^{-1}.

Refs.: (*a*) Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 1064. (*b*) This work. (*c*) Knox and Nelson, *Trans. Faraday Soc.*, 1959, **55**, 937; Pritchard, Pyke, and Trotman-Dickenson, *J. Amer. Chem. Soc.*, 1955, **77**, 2629. (*d*) Ayscough, Polanyi, and Steacie, *Canad. J. Chem.*, 1955, **33**, 743; Ayscough and Steacie, *ibid.*, 1956, **34**, 103; Ayscough, *J. Chem. Phys.*, 1956, **24**, 944; Pritchard, Pritchard, Schiff, and Trotman-Dickenson, *Trans. Faraday Soc.*, 1956, **52**, 849. (*e*) Shaw and Trotman-Dickenson, *J.*, 1960, 3210; Bérces and Trotman-Dickenson, *J.*, 1961, 348. (*f*) Trotman-Dickenson, " Gas Kinetics," Butterworths, London, 1955. (*g*) Fettis, Knox, and Trotman-Dickenson, *J.*, 1960, 4177.

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[5] Russell, *J. Amer. Chem. Soc.*, 1957, **79**, 2977.